



# Highly efficient preparation of HMF from cellulose using temperature-responsive heteropolyacid catalysts in cascade reaction

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## ABSTRACT

A series of heteropolyacid catalysts ( $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_3\text{xH}_{3-\text{x}}\text{PW}_{12}\text{O}_{40}$  (abbreviated as  $\text{Ch}_x\text{H}_{3-\text{x}}\text{PW}_{12}\text{O}_{40}$ ,  $\text{x}=1, 2$  and 3)) had been synthesized using choline chloride and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  as the raw materials, which were used as heterogeneous catalysts in one-pot conversion of cellulose to 5-hydroxymethylfurfural (abbreviated as HMF) in double solvent system containing methyl isobutyl ketone (abbreviated as MIBK) and  $\text{H}_2\text{O}$ . A remarkable HMF yield of 75.0% was achieved catalyzed by  $\text{Ch}_2\text{H}_2\text{PW}_{12}\text{O}_{40}$  within 8 h at 140 °C attributed to its higher Brønsted acidity and thermoregulate property comparable to its homogeneous form  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . To the best of our knowledge, it was almost the highest yield of HMF from cellulose by now, while the best yield of 64.0% was reported so far over  $\text{AlCl}_3$  in biphasic system. Using our biphasic reaction protocol, even raw lignocellulosic biomass straw, gave HMF yields of 27.6%. Moreover, such heteropolyacid catalysts could be recycled under simply lowering the reaction temperature to room temperature without loss of its weight, which were reused for more than 10 times.

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## 1. Introduction

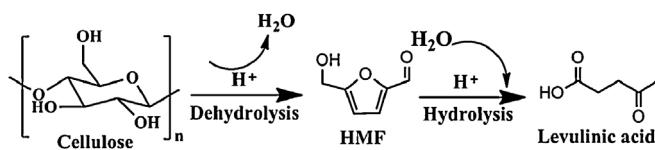
The resource shortage and global warming have attracted much attention in the transformation of biomass renewable energy into useful chemicals and fuels [1–4]. For all available biomass resources, the carbohydrates are regarded as one of the most important raw materials for the production of HMF, a very versatile platform towards fuels and chemicals [5–7]. In general, HMF is produced from monosaccharides including fructose and glucose catalyzed by acids in water or in biphasic solvents [8,9]. It is highly desirable to be able to produce HMF from cellulose or other non-edible polysaccharides, which are more abundant and low cost than edible glucose or fructose (Scheme 1). However, the yield of HMF was obtained only as high as 46.0% in aqueous solution due to rigid and insoluble structure of cellulose [10], instability of HMF in water leading to further decomposition, and formation of humins [11] (Table S1). In order to achieve higher conversion of cellulose, the mass transferring limitation between cellulose and a solid catalyst needs to be overcome. Meanwhile, it is known that HMF yield was

maximized at relatively higher temperature up to 200–300 °C and short time [12] in aqueous system, while HMF was easily decomposed to levulinic acid (LA) or formic acid. Therefore, the use of ionic liquids (ILs) as solvents was one alternative way to promote the conversion of cellulose and production of HMF [13]. Another way was to use “hybrid approach” combining the reaction and separation procedures in one unit [14], in which biphasic solvents had been used for production of HMF from various biomass [15] combined with different homogeneous and heterogeneous catalysts. The yield of HMF could be increased to 53.0% under this strategy.

Heteropolyacids (HPAs) are protonic acids with strong Brønsted acidity, which were widely applied in biomass conversion including monosaccharides and polysaccharides to HMF, LA or glucose [16–36]. In the course of studies on biomass conversion, we designed various HPAs in conversion of saccharides to HMF or LA [16–28] including homogeneous phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) to solid phosphotungstates in water or water/organic biphasic solvents.  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  is homogeneous acid catalyst in cellulose hydrolysis with 50.5% yield at 54.7% conversion. Solid  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  is active giving 95.0% HMF selectivity with 74.0% overall yield from fructose in  $\text{H}_2\text{O}/\text{MIBK}$  biphasic. Heterogeneous  $\text{Ag}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  gives 76.0% HMF yield at ~90.0% fructose conversion also in  $\text{H}_2\text{O}/\text{MIBK}$  biphasic system. Other surfactant type

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**Scheme 1.** The formation procedure of HMF and LA from cellulose.

HPAs  $\text{Cr}[(\text{DS})_2\text{PW}_{12}\text{O}_{40}]_3$  (DS represents  $\text{OSO}_3\text{C}_{12}\text{H}_{25}$  dodecyl sulfate) is most active with 52.7% yield of HMF due to its hydrophobic core formed by dodecyl group to provide a microenvironment protecting the production of HMF. Most recently, we reported that  $[(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}]_4\text{AlW}_{12}\text{O}_{40}$  presented highest efficiency in cellulose conversion to LA with 74.8% yield in  $\text{H}_2\text{O}/\text{MIBK}$  biphasic reaction system [19]. The reason why the main product is LA is contributed to that  $[(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}]_4\text{AlW}_{12}\text{O}_{40}$  owns much protons than  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , which favors for direct production of LA from fructose. And then Lewis acidity from  $\text{Al}^{3+}$  might promote the further decomposition of HMF to LA. These two synergistic effects lead to cellulose conversion mainly to LA [19]. Meanwhile,  $[\text{MIMPSH}]_2\text{PW}_{12}\text{O}_{40}$  (MIMPSH represents  $\text{C}_4\text{H}_6\text{N}_2(\text{CH}_2)_3\text{SO}_3\text{H}$ ) gives 63.0% yield of LA in water/MIBK system at  $140^\circ\text{C}$ , and such higher efficiency is contributed to its enhanced Brønsted acidity from the combination between sulfonic group and phosphotungstic acid [18]. From the above results, it can be concluded that in order to produce HMF with higher yield, HPAs must be designed to own high enough Brønsted acidity confirming cellulose hydrolysis. In other hand, their Brønsted acidity needs not too high to promote HMF further rehydrate to LA. It is therefore highly desirable to develop a robust catalytic system which can confirm highly effective production of HMF directly from cellulose under mild conditions.

Herein, we report a temperature-controlled phase-transfer catalyst system as  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  – the combination between  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and choline chloride ( $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_3\text{Cl}$ ), for the green production of HMF from cellulose. In this catalytic system, the active sites phosphotungstic acid exhibits temperature-controlled phase transfer behavior – it dissolves in hot water up to  $60^\circ\text{C}$  and functions as a highly active homogeneous catalyst to promote the hydrolysis of cellulose then to HMF. Upon cooling the reaction temperature to room temperature, the dissolved phosphotungstic acid reprecipitates and can be easily recovered by simply centrifuge treatment. Such temperature-controlled phase transfer behavior comes from the assistance of choline cation [37]. The different chain length of choline cation had been selected to vary the microenvironment of this kind of catalysts. The other effect of choline cation is to adjust the Brønsted acidity for phosphotungstic acid through varying its amounts to satisfy highly selective conversion of cellulose to HMF. In order to obtain high HMF yields using these temperature-responsive catalysts, the reaction conditions have been optimized in the biphasic solvents systems of  $\text{H}_2\text{O}$  and organic solvents. And also the influence of organic solvents on HMF yield has been investigated including MIBK, tetrahydrofuran (THF), acetone, and dimethyl sulfoxide (DMSO).

## 2. Materials and methods

### 2.1. Materials and characterization techniques

Cellulose microcrystalline (average particle size  $50\ \mu\text{m}$ ) was purchased from Beijing InnoChem Science & Technology Co., Ltd. All other reagents were of AR grade and used without further purification.  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  was prepared according to the literature method [38].

FTIR spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. The elemental analysis was tested using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400CHN

elemental analyzer. TEM micrographs were recorded on a Hitachi H-600 transmission electron microscope. The  $^{31}\text{P}$  NMR spectra of the catalysts were achieved with a Bruker AM 400 spectrometer at  $161.9\text{ MHz}$ . X-ray diffraction (XRD) patterns of the catalysts were obtained on Rigaku Dmax 2000 X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154178\text{ nm}$ ) (Rigaku Corporation). The contents of HMF and LA were obtained periodically on Agilent Technologies 7820A GC system fitted with a Agilent J&W Advanced capillary GC column.

### 2.2. Synthesis of the catalysts

The synthesis of the  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  catalysts was based on the previous literature [39].  $\text{CHCl}$  (0.467 g, 3.34 mmol) was added to the solution of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (10 g, 3.34 mmol) in 20 mL of distilled water with stirring at room temperature for 8 h. A white precipitate was formed and washed with distilled water, recrystallized twice by  $\text{CH}_3\text{CN}$  and dried at  $60^\circ\text{C}$  and then gave a white product  $\text{Ch}_2\text{HPW}_{12}\text{O}_{40}$ . The yield of the catalyst was about 70.0%. The synthetic routes of the catalysts were showed in detail in Scheme S1 of the Supporting Information. IR (KBr pellet,  $4000\text{--}400\text{ cm}^{-1}$ ): 1080.30, 978.70, 894.40, 806.04  $\text{cm}^{-1}$ . Anal. Calcd (Found) for  $\text{Ch}_2\text{HPW}_{12}\text{O}_{40}$ : C, 2.09(2.01); N, 0.43(0.47); H, 0.62(0.54); P, 0.92(1.04); and W, 72.70(73.95) %, respectively.

The other catalysts were prepared using the same procedure but different amount of  $\text{CHCl}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ .  $\text{CHCl}$  (0.934 g, 6.68 mmol) was added to the solution of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (10 g, 3.34 mmol) in 20 mL of distilled water with stirring at room temperature for 8 h and obtained the  $\text{Ch}_2\text{HPW}_{12}\text{O}_{40}$ . IR (KBr pellet,  $4000\text{--}400\text{ cm}^{-1}$ ): 1080.24, 978.82, 894.52, 806.65  $\text{cm}^{-1}$ . Anal. Calcd (Found) for  $\text{Ch}_2\text{HPW}_{12}\text{O}_{40}$ : C, 4.05(3.89); N, 1.23(0.91); H, 1.02(0.95); P, 0.89(1.00); and W, 70.55(71.48) %, respectively.

$\text{CHCl}$  (1.401 g, 10.02 mmol) was added to the solution of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (10 g, 3.34 mmol) in 20 mL of distilled water with stirring at room temperature for 8 h and obtained the  $\text{Ch}_3\text{PW}_{12}\text{O}_{40}$ . IR (KBr pellet,  $4000\text{--}400\text{ cm}^{-1}$ ): 1080.30, 978.70, 894.40, 806.04  $\text{cm}^{-1}$ . Anal. Calcd (Found) for  $\text{Ch}_3\text{PW}_{12}\text{O}_{40}$ : C, 5.72(5.65); N, 1.43(1.32); H, 1.50(1.33); P, 0.86(0.97); and W, 68.06(69.17) %, respectively.

### 2.3. Hydrolysis of the cellulose and raw lignocellulosic biomass

For hydrolysis of cellulose in double solvent of  $\text{H}_2\text{O}/\text{MIBK}$  system, a mixture of cellulose (0.1 g) and catalyst (0.11 mmol) was added into water (0.5 mL) and MIBK (5 mL). Then it was heated at  $140^\circ\text{C}$  in a steel autoclave lined with Teflon for 8 h with stirring (300 rpm). The reaction was stopped by rapidly cooling the reactor in an ice bath at  $0^\circ\text{C}$ . After cooling to room temperature, the reaction mixture was poured into a centrifuge tube to be centrifuged and it presented three layers (Fig. S1): the upper is the organic phase containing main products of HMF and little LA; the medium is aqueous phase containing glucose and fructose, the bottom is unreacted cellulose, catalyst. It could not see by-product humin due to its attaching to the wall of the reactor, which was measured as 2 mg as most of time and did not influence the conversion of cellulose significantly. Cellulose conversions (wt%) were determined by the change of cellulose weight before and after the reaction. HMF and LA were determined by GC (Gas Chromatograph).

For hydrolysis of raw lignocellulosic biomass in double solvent of  $\text{H}_2\text{O}/\text{MIBK}$  system, a mixture of raw lignocellulosic biomass (corn stover, pinewood or husk of xanthoceras) (0.1 g) and catalyst (0.11 mmol) was added into the mixture of water (0.5 mL) and MIBK (5 mL). Then it was heated at  $140^\circ\text{C}$  in a steel autoclave lined with Teflon for 10 h with stirring (300 rpm). The reaction was stopped by rapidly cooling the reactor in an ice bath at  $0^\circ\text{C}$ . After the reaction, the reaction mixture presented three layers: the upper

is the organic phase containing main products of HMF and little LA; the medium is aqueous phase containing glucose and fructose, the bottom contains unreacted cellulose, by-product humin and catalyst.

As the catalyst could not be centrifuged from the mixture of unreacted cellulose and by-product of humin, the repeated experiment were done only augmenting certain fresh cellulose to 0.1 g as starting usage. After ten cycles, the solid of unreacted cellulose, humin and catalyst was washed with water of 80 °C for three times. The temperature-control catalyst of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  was dissolved in hot water and then distilled to dry under vacuum distillation for catalyst recycling.

#### 2.4. Adsorption experiment

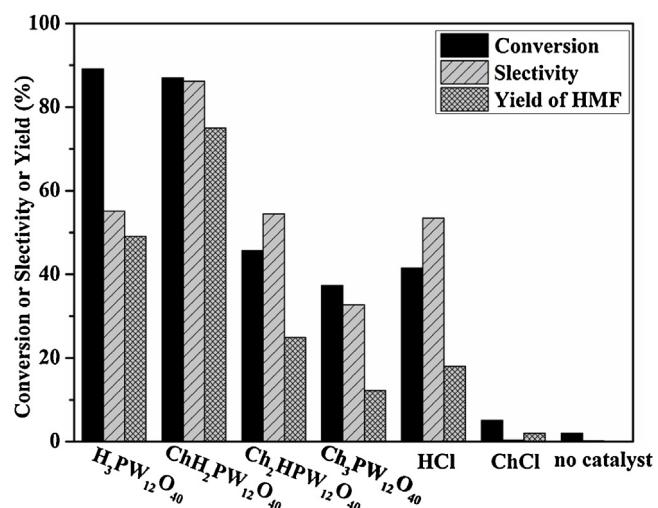
Adsorption experiment was carried out to determine the adsorption capacity of catalyst for cellulose. In the process of adsorption experiment, 0.11 mmol of catalyst and 0.1 g of cellulose were added with 5.5 mL  $\text{H}_2\text{O}$  in a steel autoclave lined with Teflon for 1 h at 140 °C. Then the steel autoclave was cooled to 80 °C to separate cellulose and catalyst, where catalyst was in aqueous phase. Then the aqueous solution was evaporated at a Rotary Evaporator to give powder, which was dried under vacuum at 60 °C then to be used in determining the adsorption effect of cellulose by IR spectroscopy.

### 3. Results and discussion

#### 3.1. Characterization

From the results of the elemental analyses of the  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ , the C, N, H, P and W contents in catalyst were C, 2.09; N, 0.43; H, 0.62; P, 0.92; W, 72.70%, respectively. Compared with the calculated values of C, 2.01; N, 0.47; H, 0.54; P, 1.04; W, 73.95%, the results were satisfactory to confirm the formation of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ .

The FTIR spectra of  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  were shown in Fig. S2, which gave the four characteristic peaks for  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ ,  $\text{Ch}_2\text{HPW}_{12}\text{O}_{40}$ , and  $\text{Ch}_3\text{HPW}_{12}\text{O}_{40}$  centered at 1080, 979, 894, and 806  $\text{cm}^{-1}$ , respectively. Compared to the pure  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  [38], the peaks belonging to the  $\nu_{\text{W-Od}}$  (terminal oxygen, 984  $\text{cm}^{-1}$ ),  $\nu_{\text{W-Oc-W}}$  (inter bridge oxygen between corner-sharing  $\text{WO}_6$  octahedra, 890  $\text{cm}^{-1}$ ), and  $\nu_{\text{W-Oe-W}}$  (intra bridge oxygen between edge-sharing  $\text{WO}_6$  octahedra, 798  $\text{cm}^{-1}$ ) shifted due to the exchanging of protons by choline cations. In addition, the peaks at 3473, 3039 and 1472  $\text{cm}^{-1}$  were attributed to C–H and C–N, respectively, showing the existence of quaternary ammonium in  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ . These results determined that the catalysts kept the original heteropolyacid Keggin structure and choline cations existed in  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ . The powder X-ray diffraction patterns were used to further demonstrate the structure of  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ . Compared to the diffraction peaks of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  showed the similar diffraction peaks (Fig. S3). This result determined the original structure of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  was kept after combination of ChCl and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  at different ratio. Meanwhile no diffraction peaks belonging to choline cation showed that the uniform of  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  formed and there was not the physical mixture between  $\text{Ch}^+$  and heteropolyacid anions. The  $^{31}\text{P}$  MAS NMR spectra (Fig. S4) of the  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ ,  $\text{Ch}_2\text{HPW}_{12}\text{O}_{40}$ , and  $\text{Ch}_3\text{PW}_{12}\text{O}_{40}$  gave one peak at -16.40, -16.53, and -16.65 ppm, respectively. Their parent  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  gives one peak at -15.6 ppm, and these shifts were ascribed to the connection organic cations with  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . This also could prove the formation of  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  and no physical mixture of ChCl and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . The different shifts of the catalysts were due to the different degree of organic group substituted.



**Fig. 1.** Effect of different catalysts on the cellulose hydrolysis. Reaction conditions: cellulose (0.1 g), water (0.5 ml), MIBK (5 ml), 140 °C, 8 h, catalyst (0.11 mmol).

From the TEM image of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ , it showed that it could form relatively uniform micellar particle about 10 nm (Fig. S5).

The Brønsted acid strength was determined by the ammonia titration reaction [40]. According to the content of the ammonia consumption, the catalytic acid strength was in the range of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (1.78 mmol/g) >  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  (0.62 mmol/g) >  $\text{Ch}_2\text{HPW}_{12}\text{O}_{40}$  (0.32 mmol/g) >  $\text{Ch}_3\text{PW}_{12}\text{O}_{40}$  (0.02 mmol/g). This was relative to the number of protons in HPAs.

#### 3.2. Catalytic activity of $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$

Hydrolysis of cellulose had been done catalyzed by different acid catalysts including no catalyst,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ ,  $\text{Ch}_2\text{HPW}_{12}\text{O}_{40}$ ,  $\text{Ch}_3\text{PW}_{12}\text{O}_{40}$ , ChCl, and HCl (Fig. 1). It can be seen that without any catalysts, cellulose almost could not be converted under our reaction conditions. Brønsted acids HCl and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  presented 41.5 and 89.2% conversion of cellulose, while ChCl and  $\text{Ch}_3\text{PW}_{12}\text{O}_{40}$  without Brønsted acidity only gave 2.0 and 12.2% conversion, respectively. For  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ , the conversion of cellulose followed the variety of Brønsted acidity, i.e.  $\text{ChH}_2\text{PW}_{12}\text{O}_{40} > \text{Ch}_2\text{HPW}_{12}\text{O}_{40} > \text{Ch}_3\text{PW}_{12}\text{O}_{40}$ . These indicated that strong Brønsted acidity of catalysts was essential for hydrolysis of cellulose.

For the yield of HMF, the different catalysts showed the different efficiency as the scope of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  (75.0%) >  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (49.1%) >  $\text{Ch}_2\text{HPW}_{12}\text{O}_{40}$  (24.9%) > HCl (18.0%) >  $\text{Ch}_3\text{PW}_{12}\text{O}_{40}$  (12.2%).  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  obtained the low HMF yield of 49.1% compared to  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ , suggesting that acid catalyst with higher Brønsted acidity may not favor for the highest yields of HMF due to the further degradation to LA.  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  gave the conversion of cellulose and the highest yield of HMF as 87.0% and 75.0% at 140 °C and 8 h, respectively. It can be seen that the cellulose conversion over  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  was comparable to homogeneous  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  but the selectivity was larger than  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . The consequence was quite significance because there were only a few successful examples so far that the catalytic effective of heterogeneous catalyst was similar to the homogeneous state [41]. The highest yield so far over  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  might be contributed to higher Brønsted acidity and the temperature-responsive property as well (Fig. 2). It can be seen that  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  is insoluble in cool water before the reaction and became into soluble in water as increasing the reaction temperature up to 60 °C. The UV-visible spectra of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  at different temperature could confirm this point (Fig. S6a). From the UV-vis spectra of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  at



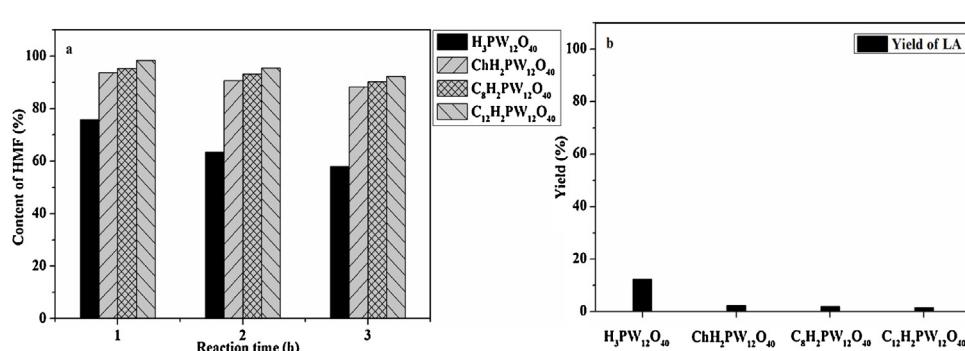
**Fig. 2.** The states of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  with the temperature change. (a) at room temperature, (b) heating to  $140^\circ\text{C}$ , and (c) cooling to room temperature.

different temperature (Fig. S6a), it can be seen that it is insoluble in water at room temperature and its solubility in water increased with enhancement of temperature from 60 to  $140^\circ\text{C}$ . Therefore, phase changing of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  occurred as varying the temperature, which was the main contribution for  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  acting as homogeneous catalysts in higher temperature. It was supposed that temperature-responsive properties came from the assistant effect of choline ions, while  $(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}$  ion interacted with water to form hydrogen-bond as increasing the temperature resulting in  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  dissolving in water. The dissolving test of the catalysts with the different amount of choline could demonstrate this phenomenon (Fig. S6b), which the transmittance of  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  increased gradually with increasing number of  $(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}^+$  in the following order as  $\text{Ch}_3\text{PW}_{12}\text{O}_{40} > \text{Ch}_2\text{HPW}_{12}\text{O}_{40} > \text{ChH}_2\text{PW}_{12}\text{O}_{40}$ .  $\text{Ch}_3\text{PW}_{12}\text{O}_{40}$  gave the biggest transmittance among  $\text{Ch}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ , indicating that three number of organic group had large effect on their temperature-responsive properties. Others similar catalysts with different organic ions such as  $[(\text{C}_8\text{H}_{17})(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{H}_2\text{PW}_{12}\text{O}_{40}$  and  $[(\text{C}_{12}\text{H}_{25})(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{H}_2\text{PW}_{12}\text{O}_{40}$  were compared to prove the impact of  $\text{Ch}^+$  on temperature-responsive performance. The visible spectra of the different chain length of catalysts were shown in Fig. S7, which solubility in water decreased with the chain length increasing at the same temperature. Longer chain length of organic cation was, lower solubility in water presented. The hydrogen bond for  $[(\text{C}_8\text{H}_{17})(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{H}_2\text{PW}_{12}\text{O}_{40}$  or  $[(\text{C}_{12}\text{H}_{25})(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{H}_2\text{PW}_{12}\text{O}_{40}$  was not strong enough for promoting their solubility in water when increasing temperature. Therefore, the conversion of cellulose over these two catalysts was only 70.0 and 51.3% under the same reaction conditions.

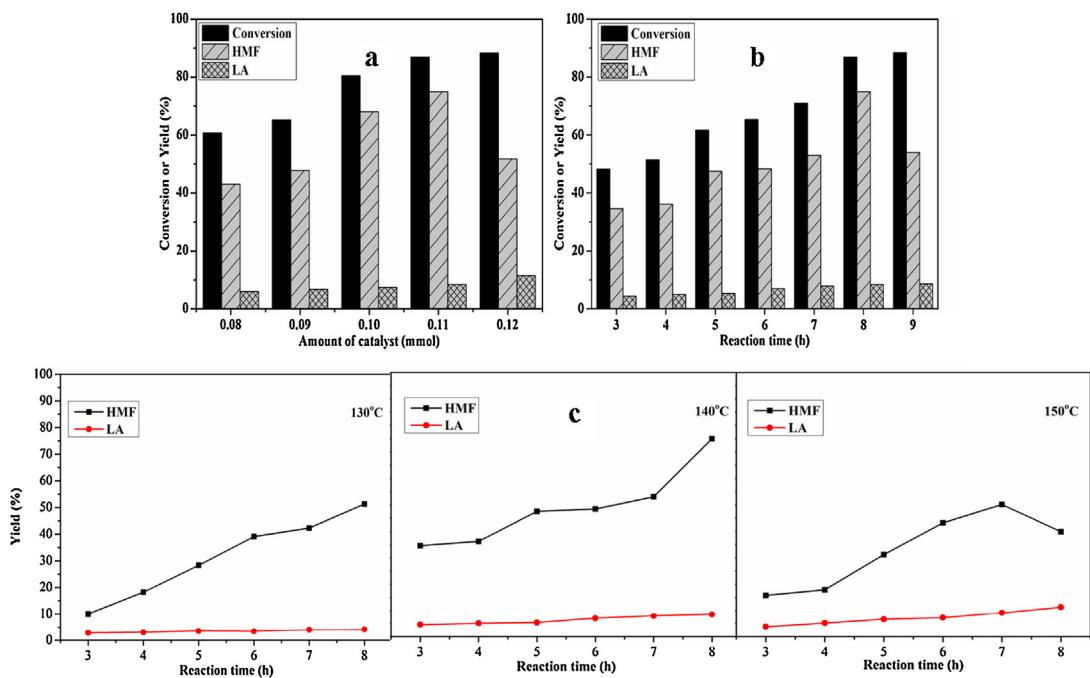
The enhanced efficiency of HMF over  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  was also attributed to the formation of nanoreactor through the self-assembly. The morphology of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  was tested by TEM (Fig. S5), showing that  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  could self-assembled as micellar spheres in water with sizes around nanometers at higher temperature. Therefore, this nanoassembly provided nanoreactor for cellulose transformation into HMF with higher conversion. The formation of nanoreactor based on  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  was expressed as amphiphilic molecules of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  self-assembled to form micelles during the reaction, which exhibited spherical structure of polar  $\text{H}_2\text{PW}_{12}\text{O}_{40}^-$  outside and  $\text{Ch}^+$  in side (Scheme S1). In hydrolysis of cellulose, such assemble could adsorb some cellulose molecules through interaction between  $\text{H}_2\text{PW}_{12}\text{O}_{40}^-$  and cellulose, hence to concentrate cellulose molecules around catalytic sites. The adsorption of cellulose by the  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  was determined by IR spectrum of the after adsorption experiment (Fig. S8). After adsorption, the peaks originated from cellulose (the skeletal vibration of C—O—C in cellulose) at  $1167.0\text{ cm}^{-1}$  shifted to  $1160.0\text{ cm}^{-1}$  and the four characteristic peaks of polyoxometalate also shifted, suggesting some interaction occurred between O atom of cellulose and the oxygen of  $\text{PW}_{12}\text{O}_{40}^{3-}$ . Therefore,  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  exhibited almost the same activity as homogeneous  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  in cellulose hydrolysis.

Another contribution to high HMF yield was the lower Brønsted acidity for  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  than for  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  [27]. It was resumed that HMF was more stable in the presence of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  than over highly acidic soluble  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . Fig. 3 showed that the decomposition of HMF into levulinic acid slowed down over  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  compared to  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . Furthermore, the higher yield of HMF was contributed to the hydrophobic environment coming from the existence of  $\text{Ch}^+$  in  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ . During hydrolysis reaction, cellulose was firstly adsorbed by hydrophilic head of  $\text{H}_2\text{PW}_{12}\text{O}_{40}^-$  and was catalyzed to glucose and further to HMF. And then, obtained HMF was protected by hydrophobic tail of  $\text{Ch}^+$  group and was extracted to organic phase by MIBK, as the less polar HMF molecule exhibits a high affinity for hydrophobic sorption sites [42]. Therefore, the further hydration of HMF to LA was limited by the protection of hydrophobic surrounding. The conversion of HMF catalyzed by  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ ,  $[(\text{C}_8\text{H}_{17})(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{H}_2\text{PW}_{12}\text{O}_{40}$ , and  $[(\text{C}_{12}\text{H}_{25})(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{H}_2\text{PW}_{12}\text{O}_{40}$  showed that HMF was more stable in the presence of catalysts with large chain organic cations due to their more hydrophobic environment (Fig. S9). Therefore, it can be concluded that the hydrophilic group of  $\text{H}_2\text{PW}_{12}\text{O}_{40}^-$  was the main contribution to concentrate cellulose, and hydrophobic group of  $\text{Ch}^+$  resulted to the limitation of HMF for further decomposition.

**Fig. 3.** At last, the temperature-responsive property provided significant benefit for separation and recovery.  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  could reprecipitate from its reaction sample as decreasing the temper-



**Fig. 3.** Stability of HMF combined with  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ ,  $[(\text{C}_8\text{H}_{17})(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{H}_2\text{PW}_{12}\text{O}_{40}$ , and  $[(\text{C}_{12}\text{H}_{25})(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{H}_2\text{PW}_{12}\text{O}_{40}$  at  $140^\circ\text{C}$  (a), and the yield of LA over different catalysts in 3 h (b).



**Fig. 4.** The effect of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  under different reaction conditions (a) amount of catalyst, (b) reaction time, and (c) temperature versus reaction time.

**Table 1**

The effect of organic solvent on the conversion of cellulose and the yields of HMF.

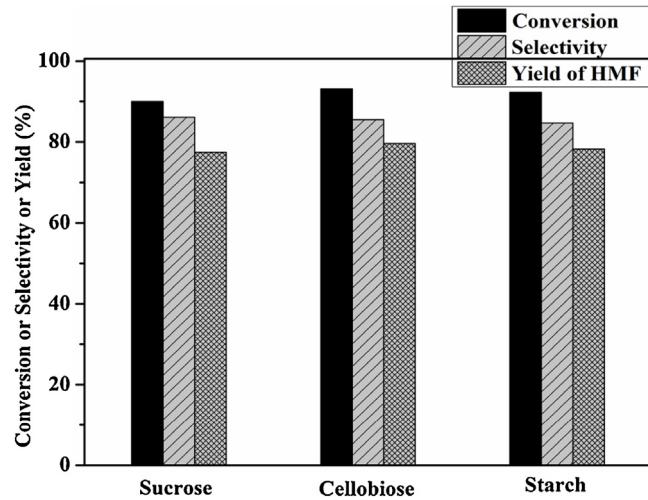
Entry	Solvent (mL)	Conversion (%)	Yield of HMF (%)
1	$\text{H}_2\text{O}$ (5.5)	17.2	5.3
2	MIBK (5.5)	70.3	49.1
3	DMSO (5.5)	61.7	40.1
4	Acetone (5.5)	50.9	34.3
5	THF (5.5)	40.3	26.2
6	MIBK (5.0)/ $\text{H}_2\text{O}$ (0.5)	87.0	75.0
7	DMSO (5.0)/ $\text{H}_2\text{O}$ (0.5)	59.5	43.8
8	Acetone (5.0)/ $\text{H}_2\text{O}$ (0.5)	56.4	39.8
9	THF (5.0)/ $\text{H}_2\text{O}$ (0.5)	45.9	29.7
10	MIBK (4.7)/ $\text{H}_2\text{O}$ (0.8)	58.7	38.8
11	MIBK (4.5)/ $\text{H}_2\text{O}$ (1.0)	37.6	18.5
12	MIBK (4.0)/ $\text{H}_2\text{O}$ (1.5)	29.3	11.4

\*Reaction conditions: cellulose (0.1 g),  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  (0.11 mmol), 140 °C, 8 h.

ature to room temperature. Thus, the cellulose hydrolysis over  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  was mainly attributed to their Brønsted acidity and thermoregulated characteristics.

### 3.3. Optimization of the reaction conditions

Firstly, different organic solvents had been evaluated for their effect on cellulose conversion including DMSO (dimethyl sulfoxide), acetone and THF (tetrahydrofuran) (Table 1) combination with water. Compared to aqueous system, the conversions and yields were enhanced significantly using biphasic solvents similar to the previous reports [15]. Meanwhile, only using organic solvent did not give higher yields of HMF in comparison to biphasic solvents, showing that water is essential for cellulose conversion because of low solubility for the substrate in organic solvents and also the requirement of hydrolysis reaction. The different solvents gave the different performance: the conversion of cellulose varied in different biphases: water/MIBK (75.0% yield at 87.0% conversion)>water/DMSO (43.8% yield at 59.5% conversion)>water/acetone (39.8% yield at 56.4% conversion)>water/THF(29.7% yield at 45.9% conversion). MIBK was most efficient solvent under our reaction conditions for cellulose into HMF with 75.0% yield of HMF at 87.0% conversion of cellulose. Assis-



**Fig. 5.** The effect of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  on different substrates hydrolysis. Reaction conditions: sucrose (0.1 g), 130 °C, 3 h; cellobiose (0.1 g), 130 °C, 3 h; strach (0.1 g), 130 °C, 5 h.

tant by MIBK, the produced HMF was extracted from aqueous phase to organic phase as soon as it formed, which prevented from further decomposition. Thus, the lower concentration of HMF in water limited the rate of side-reaction then thereby improved the HMF yields [43]. The volume ratio between MIBK to water also influenced the catalytic activity for  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ . Increasing amount of water gave decreased trend either for cellulose conversion or for HMF yields due to the decreasing of concentrations of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  resulting in lower concentration of active sites [44]. At volume ratio of  $\text{H}_2\text{O}/\text{MIBK} = 1:10$ ,  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  presented the highest yields of HMF 75.0%. Dumesic had reported that adding some sodium chloride could help to yield more HMF using HCl catalyst in biphasic solvents [8,45]. We check the effect in our system. It found that extra adding NaCl could not obviously increase the yield of HMF, showing that heteropolyacid  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  itself was a salt and could assist the produce of HMF.

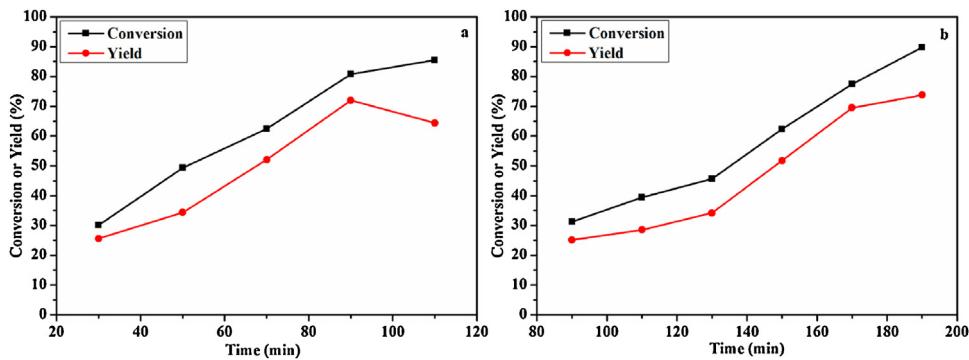


Fig. 6. The effect of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  on cellulose hydrolysis under microwave assistance (a) 140 °C at different reaction time. (b) 110 °C at different reaction time.

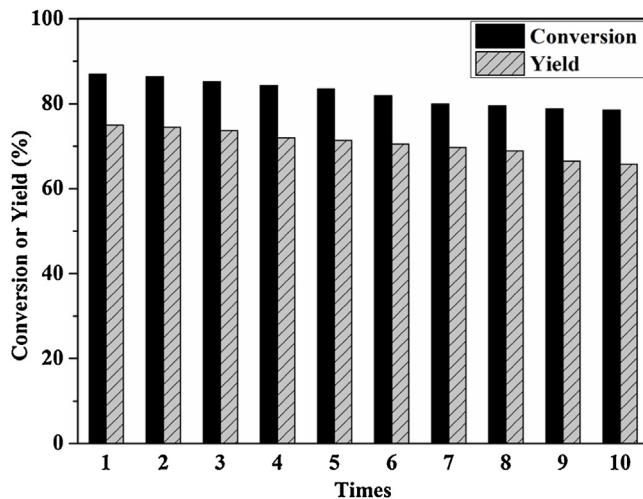


Fig. 7. The recycle tests of the catalyst. Reaction conditions: cellulose (0.1 g),  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  (0.11 mmol), water (0.5 mL), MIBK (5 mL), 140 °C, 8 h.

For further optimizing the cellulose hydrolysis process with the  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ , the reaction was performed at different amount of catalyst, reaction times and temperatures. The conversion of cellulose and the yields of HMF and LA at the different amount of catalyst were presented in Fig. 4a. With the increase of catalyst dosage from 0.08 to 0.11 mmol, cellulose conversions and the yields of HMF were increasing from 60.8 and 43.0% to 87.0 and 75.0%, respectively. The result could be owing to the increase of the catalytically active sites of the catalysts [46]. While the amount of catalyst increased to 0.12 mmol, the conversion of cellulose was not improved significantly, but the yields of HMF decreased sharply to 51.8%. This decrease trend was attributed to higher acid site leading to further decomposition of HMF to LA. It is obvious that the amount of 0.11 mmol was selected to be the most appropriate dosage with high HMF yield. Reaction time also can affect the hydrolysis of cellulose and the yields of HMF and LA at different reaction time were shown in Fig. 4b. The result proved that increasing the reaction time from 3 to 8 h can obtained the increasing conversion of cellulose and yields of HMF from 48.2 to 87.0% and 34.6–75.0%, respectively. Extending the reaction time to 9 h did not give improved conversion but lowing yield due to the existence of side reactions. A plot of the cellulose conversion and HMF yield as function of the reaction temperature was shown in Fig. 4c. Under the reaction conditions with 0.1 g of cellulose, 0.11 mmol of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  and 8 h reaction time, the yield of HMF increased from 10.0% at 130 °C to 75.0% at 140 °C. A further enhancement of temperature to 150 °C resulted in a sharp decrease in yield to 39.9%, which was also supposed to the side-reactions be predominant at higher temperature. To the

best of our knowledge, the reported catalysts in the hydrolysis of cellulose to HMF (Table S1) present the highest yields of 64.0% in ionic liquid ([BMIM]Cl) catalyzed by  $\text{AlCl}_3$ . For solid acid catalyst,  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  is most active among the previous reports by now under reaction conditions with 8 h and 140 °C.

The scope of this study was further extended to examine the conversion of cellobiose (a dimer of glucose), sucrose (a dimer of fructose and glucose units) and starch (a polysaccharide consisting of hundreds of glucose units) (Fig. 5) over  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  in the double solvents. It can be seen that almost all polysaccharides were converted and as high as 77.5, 79.6 and 78.2% yields of HMF were obtained from sucrose, cellobiose and starch, respectively. It is obvious that the novel temperature self-control catalyst of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  has a very high activity in the process of biomass conversion. To delight,  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  could catalyze the conversion of intact lignocellulosic biomass including corn stover, pinewood and husk of xanthoceras to produce HMF with 27.6, 11.6, and 13.1% yields, respectively.

By now, hydrolysis of cellulose into chemicals over HPA catalysts had been done under microwave reaction [47], which is the efficient way to release the reaction conditions as well as increase the efficiency compared to the conventional reactions. Therefore, the conversion of cellulose over  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  had been checked under microwave assistance (Fig. 6). The yields of HMF under microwave assistance could reach 72.0% at 140 °C within 90 min, showing that the higher efficiency of microwave reaction (Fig. 6a). Further increasing of reaction time did not improve HMF yield at 140 °C but give decreasing trend. At 110 °C, conversion and HMF yield were obtained as 89.5%, 73.8% at 190 min (Fig. 6b). It can be concluded that microwave could assist cellulose convert into HMF within short time and at lower temperature compared to traditional heating.

### 3.4. The recycle of the catalyst

According to the described above, the catalyst could be separated from the reaction mixture simply by cooling the temperature (Fig. 2c) using its temperature-responsive property. The recovery effect of the catalyst was about 94.3% and the leaching amount was only 5.7% of initial amount after ten cycles.  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  could not dissolve in MIBK or water under room temperature, which is in solid phase. In order to check the nature of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$ , the leaching test had been done [48]: the catalyst was filtered coolly after reaction 3 h (ca. 48.2% conversion and 34.6% HMF yield) and the filtrate mixed with 0.052 g cellulose to react further 1 h at the same temperature of 140 °C. The conversion of cellulose was only 0.8%, which showed a little dissolving of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  into mixture after cooling the reaction temperature. The above filtrate was checked by UV-vis spectroscopy to determine the leaching of  $\text{ChH}_2\text{PW}_{12}\text{O}_{40}$  into reaction mixture, showing that leaching amount was only 0.1%.

$\text{CH}_2\text{PW}_{12}\text{O}_{40}$  can be recycled more than 10 times without significant loss in the cellulose conversion or HMF yield (Fig. 7) with only loss of activity and yield as 8.5 and 9.2%, respectively. The excellent reusability can be attributed, on the one hand, to the temperature – responsive property. The IR spectrum of the catalyst after ten times reaction showed that the catalyst still kept the original Keggin structure (Fig. S10b).  $\text{CH}_2\text{PW}_{12}\text{O}_{40}$  was found to be rather stable under hydrothermal reaction conditions, which is the main contribution to its exceptional reusability.

#### 4. Conclusions

A series of  $\text{CH}_{x}\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  catalysts had been synthesized using choline chloride and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  as building blocks, which exhibited temperature-responsive property and certain Brønsted acidity.  $\text{CH}_2\text{PW}_{12}\text{O}_{40}$  exhibited almost the highest activity (87.0% of conversion and 75.0% of HMF yield) among the previously reported catalysts. Such highest efficiency in one-pot production of HMF from cellulose over  $\text{CH}_2\text{PW}_{12}\text{O}_{40}$  was attributed to its homogeneous behavior as enhancement of reaction temperature, not higher Brønsted acidity allowing no further degradation of HMF to LA, extraction of HMF from the reaction solution by MIBK preventing HMF further reshydration, and hydrophobic surrounding protecting HMF from further degradation. This could give us some useful advice in designation of HPA catalysts in cellulose conversion targeting to required products. Moreover, temperature-responsive property and high stability gave benefit in recovery and reuse for ten times without significant loss of activity.  $\text{CH}_2\text{PW}_{12}\text{O}_{40}$  was also active in production of HMF from other polysaccharides and some crude lignocellulosic biomass, showing wide application. In addition, microwave-assistance could improve the yields of HMF within short time and relatively low temperature.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.05.019>.

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